(Z,Z)-1,3-Butadiene-1,4-dithiol (8). Sodium (100 mg, 4.3 mmol) was added to liquid NH_3 (15 mL) at –75 °C and **6a** (300 mg, 1.01 mmol) was added all at once.After stirring for 1 h, NH_3 was removed, ether (20 mL) and H_2SO_4 solution (20%, 5 mL) was added at –20 °C [all aqueous solutions were deoxygenated with argon prior to use]. The ether layer was separated and the aqueous layer was extracted with ether (50 mL); the combined orgainc layers were extracted with KOH solution (2%, 2 × 30 mL), which after acidification with H_2SO_4 solution (2%) was extracted with ether (2 × 30 mL). The ether soltuion was dried at 0 °C, filtered and concentrated in vacuo to afford **8** as a pale yellow oil (36 mg, 30% yield estimated by ^{1}H NMR; ^{1}H NMR δ 6.42 (dd, J = 6.6, 1.8 Hz, 2H), 6.20 (m, 2H), 2.96 (d, J = 8.7 Hz, 2H); ^{13}C NMR δ 123.22, 118.34.

(Z,Z)-1,4-Bis(benzylthio)-1,4-diphenyl-1,3-butadiene (11c). Powdered KOH (0.026 g, 0.46 mmol) was added to a stirred solution of 1,4-diphenyl-1,3-butadiyne (0.500 g, 2.47 mmol) and α-mercaptotoluene (0.645 g, 5.19 mmol) in DMF (10 mL) and MeOH (2.5 mL) at 0 °C. After 5 h at 25 °C, ether (50 mL) was added, the solution was washed with brine (5 × 15 mL), and water (10 mL), dried, filtered, and concentrated. Recrystallization of the residue (4:1 CH_2Cl_2:MeOH) gave the known title compound as a yellow solid (0.612 g, 55%); ^{1}H NMR δ 7.55-7.16 (m, 16H), 7.14 (s, 2H), 7.06-7.01 (m, 4H), 3.62 (s, 4 H); ^{13}C NMR δ 140.00, 133-126 (several), 36.61.

3,6-Diphenyl-1,2-dithiin (1d). Lithium (30 mg, 4.3 mmol) was added to liquid NH_3 (20 mL) at -80 °C. After all the lithium had reacted, compound **11c** (200 mg, 0.44 mmol) in THF (4 mL) was added dropwise with stirring. The mixture was stirred for 2.5 h at -65 °C, quenched with MeOH, warmed to 25 °C, and concentrated in vacuo. At 0 °C, the

residue was mixed with ether (15 mL) and water (10 mL), and then slowly oxidized by addition of KI_3 solution (4 mL; from 225 mg I_2 [0.89 mmol] and 1.5 g KI [5.1 mmol]). The ether layer was separated, the aqueous layer extracted with ether (2 × 20 mL), the combined red organic layers washed with $Na_2S_2O_3$ (3 × 10 mL) and NH_4Cl (2 × 10 mL), dried, filtered, concentrated in vacuo, and chromatographed (1:20 CH_2Cl_2:hexanes) giving red crystals of **1d** (207 mg, 70% yield), mp 142 °C; NH_3 CI-MS *m/z* 268 (M^+); UV (CH_2Cl_2) λ_{max} 210 (1.4×10^5), 236 (7.6×10^4), 306 (6.1×10^4), 464 (ε 1.3×10^4) nm; ^{1}H NMR δ 7.8-7.1 (m, 10H), 6.91 (s, 2H); ^{13}C NMR δ 136.75, 134.82, 128.91, 128.69, 127.82, 126.08.

Benzylthioethyne. A hexane solution of *n*-BuLi (28.3 mL, 71 mmol, 2.5 *M*) was added to a stirred solution of trimethylsilylethyne (7.0 g, 71 mmol) in ether (100 mL) at -78 °C. The solution was warmed to -20 °C during 2 h, cooled to -70 °C, and treated with powdered sulfur (2.3 g, 72 mmol) from a flask connected to the reaction vessel with Gooch tubing. The solution was warmed to 10 °C, treated with benzyl bromide (8.5 mL, 72 mmol), stirred overnight, and then quenched with NH_4Cl solution (30 mL). The mixture was extracted with ether (3 × 50 mL), the combined ether layers washed with brine (30 mL) and water (30 mL), dried, filtered, and concentrated in vacuo. Without further purification the resultant yellow oil (GC-EI-MS *m/z* 220 (M^+)) was dissolved in THF (150 mL), mixed with water (10 mL) and a solution of tetra-*n*-butylammonium fluoride (TBAF, 20.4 g, 78 mmol) in THF (100 mL) and stirred for 2.5 h. The mixture was washed with brine (3 × 50 mL), dried, filtered, concentrated in vacuo and distilled (39-42 °C/0.015 mmHg) to afford the title compound as a yellow oil (10 g, 96%); ^{1}H

NMR (acetone-d_6) δ 7.5-7.25 (m, 5H), 4.05 (s, 2H), 3.38 (s, 1H); ^{13}C NMR (acetone-d_6) δ 137.89, 129.93, 129.38, 128.56, 85.43, 74.82, 40.07; IR (ν_{max}, neat) 3286, 2041 cm^{-1} (C≡C).

(*Z*,*Z*)-2,5-Bis(benzylseleno)-2,4-hexane-1,6-diol (11c). A suspension of dibenzyl diselenide (1.36 g, 4 mmol) in degassed EtOH (15 mL) at 0 °C was treated with $NaBH_4$ (0.46 g, 12 mmol) in small portions, 1,6-hexa-2,4-dienediol (**4e**; 0.22 g, 2 mmol) was added, the mixture was refluxed for 6 h, cooled to 25 °C, diluted with hexane (30 mL), filtered through a pad of silica gel, rinsed with ethyl acetate and hexane (20 mL, 1:1), and concentrated. Chromatography (1:2 ethyl acetate:hexane) gave **11c** (0.60 g, 66%) as colorless needles, mp 87.5-88 °C; ^{1}H NMR δ = 7.25 (m, 10H), 6.85 (s, 2H), 4.16 (s, 4H), 3.92 (s, 4H), 1.79 (s, 2H); ^{13}C NMR δ 138.81, 137.28, 132.36, 128.97, 128.58, 127.00, 68.08, 30.22.

3-Hydroxymethyl-6-methyl-1,2-diselenin (5d) and 3,6-Dimethyl-1,2-diselenin (5e). Lithium (0.42 g, 60 mmol) in small pieces was added to a solution of **11c** (1.35 g, 3 mmol) in liquid NH_3 (100 mL) in a 250-mL 3-necked flask at –78 °C. The blue solution was stirred overnight at –60 °C, quenched (MeOH, 10 mL), and evaporated in a stream of argon. The residue was dissolved in degassed aqueous KOH solution (10%; 180 mL) under argon which was then extracted with degassed hexane (3 × 30 mL) to remove toluene. The aqueous layer was covered with hexane (90 mL) and oxygen bubbled through the solution until the hexane phase turned red. The extraction was repeated twice with fresh hexane (2 × 90 mL) and the combined hexane extracts were dried (Na_2SO_4), concentrated, and chromatographed (1:2 ethyl acetate:hexane) to give a more polar

product (**5d**; 29%) and a less polar product (**5e**; 27%). Compound **5d** (a red oil): ^{1}H NMR δ 6.26 (d, *J* = 6.5 Hz, 1H), 6.14 (d, *J* = 6.5 Hz, 1H), 4.34 (s, 2H), 2.20 (s, 3H), 2.06 (s, 1H); ^{13}C NMR δ 128.38, 127.98, 127.73, 127.39, 66.69, 25.66; ^{77}Se NMR δ 185.2, 177.6 (vs. Me_2Se); UV ($CDCl_3$) λ_{max} = 474 nm. Compound **5e** (a red oil): ^{1}H NMR δ 6.06 (s, 2H), 2.19 (s, 6H); ^{13}C NMR δ 128.67, 123.71, 25.41; ^{77}Se NMR δ 205.8 (vs. Me_2Se); UV (hexane) λ_{max} = 478 nm (155).

(*Z*,*Z*)-1,4-Diiodo-1,4-bis(*t*-butyl)-1,3-butadiene (22a). To a stirred solution of Ti(O*i*-Pr)$_4$ (4.8 mmol, 1.5 mL) in ether (30 mL) was successively added 3,3-dimethyl-1-butyne (**20a**; 8.0 mmol, 1.0 mL) and *i*-PrMgCl (9.6 mmol, 4.8 mL, 2.0 M in ether) in this order at -78 °C. The solution was stirred at -78 °C for 1 h and at -30 °C for 2 h. The solution was then cooled below -60 °C, and iodine (8.0 mmol, 2.0 g) was added. The reaction mixture was warmed to 25 °C over 1.5 h, stirred for 0.5 h, cooled to 0 °C, slowly quenched with 1 N HCl, and extracted with pentane and ether (1:1). The organic layer was washed ($NaHSO_3$, $NaHCO_3$ and brine solutions), dried, and concentrated *in vacuo*. Recrystallization (EtOH) gave **22a** (1.55 g, 93%) as a light yellow solid, mp 74-75 °C; ^{1}H NMR δ 6.53 (s, 2H), 1.25 (s, 18H); ^{13}C NMR δ 134.43, 130.83, 41.23, 30.63; GC-MS *m/z* 418 (M^+), 291 (M-127(I)), 149, 121, 57. Anal. Calcd for $C_{12}H_{20}I_2$: C, 34.47; H, 4.82. Found: C, 34.71; H, 4.91.

(*Z*,*Z*)-1,4-Bis(benzylthio)-1,4-bis(*t*-butyl)-1,3-butadiene (23a). To a solution of **22a** (0.84 g, 2.0 mmol) in ether (30 mL) was added, with stirring, *n*-butyllithium (4.0 mmol, 1.6 mL, 2.5 M in hexane) at -78 °C over a period of 1 h. The solution was stirred at -78 °C for 2 h, and at 25 °C for 15 min, cooled to -78 °C and treated with dibenzyl disulfide

(0.97 g, 4.0 mmol) in THF (5 mL), added via syringe. The mixture was stirred for 0.5 h at -30 °C, slowly warmed to 25 °C and stirred for another 0.5 h, quenched with 1 N NaOH solution (20 mL) and extracted with ether (2 × 30 mL). The ether solution was washed (NH_4Cl and brine solutions), dried, and concentrated *in vacuo*. Recrystallization (EtOH) afforded **23a** as a white solid (0.72 g, 88%), mp 83-84 °C; ^{1}H NMR δ 7.28 (m, 10H), 7.10 (s, 2H), 3.80 (s, 4H), 1.18 (s, 18H); ^{13}C NMR δ 149.72, 130.62, 129.03, 128.50, 127.14, 41.80, 39.81, 29.37; GC-MS *m/z* 288 (M^+-122), 197, 141, 91, 57. Anal. Calcd for $C_{26}H_{34}S_2$: C, 76.04; H, 8.34. Found: C, 76.13; H, 8.53.

2,5-Bis(*t*-butyl)-thiophene (3g).[17a] Compound **1g** (10 mg) in CD_2Cl_2 (0.6 mL) in an NMR tube was cooled to -50 °C with dry ice/acetone in a Dewar flask and irradiated with visible light for 5 min. After warming to 25 °C, **3g** was the only product present (100% yield as determined by ^{1}H NMR spectroscopy); ^{1}H NMR (CD_2Cl_2) δ 6.58 (s, 2H), 1.34 (s, 18H)(lit.[17a] δ 1.33, 6.45); ^{13}C NMR (CD_2Cl_2) δ 154.21 (*C*H=), 120.18, 34.35, 32.47; EI-GC-MS *m/z* 196 (M^+), 181, 166, 151, 97, 91, 77, 57; UV (CH_2Cl_2) λ_{max} 296 (ε 8500), 266 (ε 8550), 238 nm (ε 8430).

3-Methyl-1-butyne (20b). Prepared from 1,1-dibromo-3-methyl-1-butene via the Corey-Fuchs procedure (Corey, E.J.; Fuchs, P.L. *Tetrahedron Lett.* **1972**, *36*, 3769-72). CBr_4 (132.8 g, 0.4 mol) was added slowly at 0 °C to a mixture of Ph_3P (104.8 g, 0.4 mol) and zinc dust (26.0 g, 0.4 mol) in CH_2Cl_2 (500 mL) under argon. The mixure was stirred at 25 °C for 24 h, treated with isobutyraldehyde (14.4 g, 0.2 mol) and stirred for 2 h. Pentane was added, and the mixture was filtered, the precipitate washed with CH_2Cl_2 (200 mL) and pentane (800 mL) and the combined filtrates were concentrated in vacuo.

Distillation (57-59 °C/45 mm Hg) gave 1,1-dibromo-3-methyl-1-butene as a colorless liquid (35.6 g, 78%); ^{1}H NMR δ 6.19 (d, J = 9.1 Hz, 1H), 2.57 (m, 1 H), 1.00 (d, J = 6.6 Hz, 6H); ^{13}C NMR δ 145.15, 86.87, 33.16, 21.19. *n*-BuLi (40 mL, 80 mmol, 2 M in cyclohexane) was added at 0 °C to a solution of 1,1-dibromo-3-methyl-1-butene (9.12 g, 40 mmol) in cyclohexane (120 mL). The mixture was stirred at 0-5 °C for 1 h and at 25 °C for 1 h. Hydrolysis at 0 °C and double distillation (bp range 28-42 °C) gave **20b** as a mixture with cyclohexane (6.6 g). Through ^{1}H NMR spectroscopic analysis (durene internal standard), the concentration of **20b** in cyclohexane was found to be 48%, corresponding to 92% yield; ^{1}H NMR δ 2.57 (m, 1H), 2.03 (s, 1H), 1.20 (d, J = 6.6 Hz, 6H).

2,5-Bis(trimethylsilyl)thiophene (3i)[17b]. Compound **1i** (10 mg) in CD_2Cl_2 (0.6 mL) in an NMR tube was cooled to -50 °C with dry ice/acetone in a Dewar flask and irradiated with visible light for 8 min. After warming to room temperature, **3i** was obtained in 100% yield (NMR analysis). ^{1}H NMR (CD_2Cl_2) δ 6.98 (s, 2H), 0.11 (s, 18H); ^{13}C NMR (CD_2Cl_2) δ 140.3, 134.6, -0.2; *m/z* 228 (M^+), 213, 163, 115, 99, 83, 73, 69, 55.

2,5-Bis(*t*-butyl)selenophene (36). In a similar procedure given for **3g**, **5b** (10 mg) in CD_2Cl_2 (0.6 mL) in NMR tube was cooled to -50 °C with dry ice/acetone in a Dewar flask and irradiated with visible light for 12 min. After warming to 25 °C, **36** was obtained (100% yield by NMR analysis); ^{1}H NMR (CD_2Cl_2) δ 6.74 (s, 2H), 1.35 (s, 18H); ^{13}C NMR (CD_2Cl_2) δ 162.40, 122.37, 36.30, 33.03; ^{77}Se NMR (CD_2Cl_2) δ 565; EI-LC-MS *m/z* 244 (M^+, 25%), 229 (100%); UV (CH_2Cl_2) λ_{max} 262 (ε 1400), 235 (ε 1450), 210 nm (ε 1300).[28d]

3,6-Bis(hydroxymethyl)-1,2-dithiin 1-Oxide (38e). As in the synthesis of **38c**, 3,6-bis(hydroxymethyl)-1,2-dithiin (**1e**; 88 mg, 0.5 mmol) in CH_2Cl_2 (10 mL) was treated with *m*CPBA (150 mg, 57-86%) at 0 °C. Workup and chromatography (1:1 hexane: EtOAc) gave **38e** as a light brown oil (58 mg, 62% yield); ^{1}H NMR (acetone-d6) δ 7.04 (d, J = 7.4 Hz, 1H), 6.92 (d, J = 7.3 Hz, 1H), 4.67 (d, J = 2.7 Hz, 1H), 4.49 (s, 1H); ^{13}C NMR δ 138.00, 133.65, 123.86, 118.52, 65.62, 63.51; CI LC-MS *m/z* 193 (M^++ 1); IR (ν_{max}, neat) 3358, 1652, 1045 (s; S=O) cm^{-1}.

3,6-Dimethyl-1,2-dithiin 1-Oxide (37f). As in the synthesis of **37c**, **1f** (50 mg, 0.69 mmol) in CH_2Cl_2 (20 mL) was oxidized with *m*CPBA (100 mg, 57-86%) at 0 °C. Workup and chromatography (7:3 hexane:EtOAc) gave **37f** as a light brown oil (27 mg, 48% yield); ^{1}H NMR δ 6.69 (d, J = 7.5 Hz, 1H), 6.61 (d, J = 7.5 Hz, 1H), 2.48 (s, 3H), 2.34 (s, 3H); ^{13}C NMR δ 129.97, 125.87, 124.87 (=*C*H), 119.82 (=*C*H), 24.06, 20.91; CI LC-MS *m/z* 161 (M^++ 1; 100%); IR (ν_{max}, neat) 1072 (s; S=O) cm^{-1}.

3,6-Dimethyl-1,2-dithiin 1,1-Dioxide (38f). As in the synthesis of **38c**, **1f** (50 mg, 0.69 mmol) in CH_2Cl_2 (20 mL) was treated with *m*CPBA (150 mg, 57-86%) at 0 °C. The mixture was stirred overnight at 25 °C, concentrated, and chromatographed (4:1 hexane: EtOAc) giving **38f** as a light brown oil (9.3 mg, 17% yield); ^{1}H NMR δ 6.54 (d, J = 8.01 Hz, 1H), 6.38 (d, J = 6.8 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H); ^{13}C NMR δ 130.30, 119.16, 24.38, 15.27; CI LC-MS *m/z* 193 (M^++ 1); IR (ν_{max}, neat) 1306, 1129 (s; SO_2) cm^{-1}.

3,6-Bis(thiocyanato)-2,7-dimethyl-2,6-octadiene (29a). As in the synthesis of **25a**, thiocyanogen (4.0 mmol) in CH_2Cl_2 (10 mL) was added dropwise at -78 °C to a solution prepared from Ti(O*i*-Pr)$_4$ (2.4 mmol, 0.75 mL) in ether (20 mL), 3-methyl-1,2-butadiene

(4 mmol, 0.28 mL) and *i*-PrMgCl (4.8 mmol, 2.4 mL, 2.0 M in ether) at -78 °C. Workup and chromatography (ether/hexane) gave **29a**, a white solid (0.43 g, 85%), mp 69-70 °C; ^{1}H NMR δ 2.72 (s, 4H), 1.97 (s, 6H), 1.91 (s, 6H); ^{13}C NMR δ 143.26, 116.85, 110.86, 32.44, 23.46, 21.69; GC-MS *m/z* 252 (M^+), 194, 167, 126 105, 85, 67, 53; IR (ν_{max}, neat) 2150 cm^{-1}. Anal. Calcd for $C_{12}H_{16}N_2S_2$, C, 57.11; H, 6.39. Found, C, 57.10; H, 6.35.

3,6-Bis(isopropylidene)-1,2-dithiacyclohexane (30a). Method I: As in the synthesis of **1g**, method II, **29a** (0.5 mmol, 127 mg) in THF (5 mL) was treated with SmI_2 (1.1 mmol) in THF (35 mL). After workup, chromatography (hexane) gave the known **30a** (60 mg, 60%) as a light yellow solid, mp 87-88 °C (literature[20d] 88-89 °C); ^{1}H NMR δ 2.70 (s, 4 H); 1.84 (s, 6H), 1.74 (s, 6H); ^{13}C NMR δ 129.04; 126.47, 22.09, 20.78; EI-GC-MS *m/z* 200 (M^+, 100%), 167 (68%), 153 (26%), 125 (77%), 91 (24%), 85 (56%), 67 (48%); UV (CH_2Cl_2) λ_{max} 320 (ε 1450), 266 (ε 1380), 238 nm (ε 1290).

Method II. As in the synthesis of **1g**, Method III, **29a** (0.65 mmol, 165 mg) in THF (30 mL) was treated with TBAF (1.5 mmol, 1.5 mL, 1.0 M TBAF in THF). Chromatography (hexane) gave **30a** (115 mg, 88%).

3,6-Bis(selenocyanato)-2,7-dimethyl-2,6-octadiene (29b). As in the synthesis of **22a** and **25a**, selenocyanogen (4.0 mmol) in THF (10 mL) was added dropwise at -78 °C to a solution prepared from Ti(O*i*-Pr)$_4$ (7.2 mmol, 2.3 mL) in ether (60 mL), 3-methyl-1,2-butadiene (12 mmol, 1.2 mL) and *i*-PrMgCl (14.4 mmol, 7.2 mL, 2.0 M in ether) at -78 °C. After workup, chromatography gave **29b** as a light yellow solid (1.08 g, 52%), mp 73-74 °C; ^{1}H NMR δ 2.82 (s, 4H); 1.97 (s, 6H), 1.93 (s, 6H); ^{13}C NMR δ 142.21; 118.51, 101.36, 35.10, 25.62, 21.23; GC-MS *m/z* 348 (M^+), 294, 242, 216, 173, 147, 121, 105,

91; IR (ν_{max}, neat) 2150 cm^{-1}. Anal. Calcd for $C_{12}H_{16}N_2Se_2$, C, 41.63; H, 4.66. Found, C, 42.03; H, 4.65.

3,6-Bis(isopropylidene)-1,2-diselenacyclohexane (30b) and 2,5-Bis(isopropylidene)selenolane (33b). Method I. As in the synthesis of **1g**, method II, **29b** (0.5 mmol, 175 mg) in THF (5 mL) was treated with SmI_2 (1.1 mmol) in THF (35 mL). After workup, chromatography (hexane) gave a mixture of **30b** and **33b** in a ratio of 4:3 (by ^1H NMR) as a light yellow oil. Compound **30b**: ^1H NMR δ 2.78 (s, 4H), 1.88 (s, 6H), 1.79 (s, 6H); ^{13}C NMR δ 130.24, 123.24, 33.34, 24.66, 20.76; ^{77}Se NMR δ 326.2; EI-GC-MS *m/z* 295 (M^+, 23%), 216 (46%), 67 (100%); UV (CH_2Cl_2) λ_{max} 390 nm. Compound **33b**: ^1H NMR ($CDCl_3$; δ, ppm): 2.62 (s, 4H); 1.78 (s, 6H), 1.71 (s, 6H); ^{13}C NMR δ 132.08, 122.83, 35.59, 25.60, 20.69; ^{77}Se NMR δ 355; EI-GC-MS *m/z* 216 (M^+), 214, 212, 173, 148, 133, 119, 107.

Method II. As in the synthesis of **1g**, method III, **29b** (0.5 mmol, 175 mg) in THF (3 mL) was treated with TBAF (0.5 mmol, 1.1 mL, 1.0 M TBAF in THF) in THF (15 mL). Chromatography (hexane) gave a mixture of **30b** and **33b** in a 4:1 ratio (by ^1H NMR).

3,6-Bis(thiocyanato)-2,7,7,-trimethyl-2,5-octadiene (31a). As in the synthesis of **25a**, thiocyanogen (4.0 mmol) in CH_2Cl_2 (10 mL) was added dropwise at -78 °C to a solution prepared from Ti(O*i*-Pr)$_4$ (2.4 mmol, 0.75 mL) in ether (20 mL), 3,3-dimethylbutyne (**20a**; 2.0 mmol, 0.25 mL), 3-methyl-1,2-butadiene (**26**, 2.0 mmol, 0.14 mL) and *i*-PrMgCl (4.8 mmol, 2.4 mL, 2.0 M in ether) at -78 °C. After workup, chromatography (hexane/ether) gave **31a** as a light yellow solid (0.15 g, 56%). ^1H NMR δ 6.12 (t, J = 6.5 Hz, 1H), 3.62 (d, J = 6.5 Hz, 2H), 2.03 (s, 3H), 1.92 (s, 3H), 1.22 (s, 9H);

^{13}C NMR δ 145.29, 139.08, 134.10, 115.15, 111.19, 110.71, 39.86, 36.18, 28.77, 23.71, 21.97; IR (ν_{max}, neat) 2155 (SC≡N) cm^{-1}.

3-*t*-Butyl-6-isopropylidene-1,2-dithiacyclohex-3-ene (32a). As in the synthesis of **1g**, method II, **31a** (0.5 mmol, 133 mg) in THF (4 mL) was treated with SmI_2 (1.1 mmol, 0.1 M solution in THF) in THF (35 mL) at 0 °C. After workup, chromatography (hexane) gave **32a** as a light yellow oil (80 mg, 78%). ^{1}H NMR δ 6.12 (t, *J* = 5.8 Hz, 1H), 3.11 (d, *J* = 5.8 Hz, 2H), 1.83 (s, 3H), 1.80 (s, 3H), 1.17 (s, 9H); ^{13}C NMR δ 155.02, 131.06, 126.10, 125.51, 38.04, 31.73, 28.91, 23.45, 21.28; EI-GC-MS *m/z* 214 (M^+, 32%), 181 (72%), 166 (47%), 125 (51%), 57 (100%); UV (CH_2Cl_2) λ_{max} 316 (ε 1460), 268 (ε 1430), 238 (ε 1370) nm.

3,6-Bis(selenocyanato)-2,7,7-trimethyl-2,5-octadiene (31b). As in the synthesis of **22a** and **25a**, selenocyanogen (24 mmol) in THF (55 mL) was added dropwise at -78 °C to a solution prepared from Ti(O*i*-Pr)$_4$ (14.4 mmol, 4.5 mL) in ether (120 mL), 3,3-dimethylbutyne (**20a**; 12 mmol, 1.5 mL), 3-methyl-1,2-butadiene (26, 12 mmol, 1.2 mL) and *i*-PrMgCl (28.8 mmol, 14.4 mL, 2.0 M in ether) at -78 °C. After workup, chromatography (hexane/ether) afforded **31b** (1.3 g, 30%) as a yellow solid, mp 88-89 oC; 1H NMR (6.00 (t, *J* = 6.5 Hz, 1H), 3.74 (d, *J* = 6.5 Hz, 2H), 2.04 (s, 3H), 1.96 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (143.80, 141.52, 133.78, 116.60, 101.68, 101.45, 40.37, 40.30, 29.24, 25.88, 21.55; IR (ν_{max}, neat) 2145 (SeC≡N) cm^{-1}.

3-*t*-Butyl-6-isopropylidene-1,2-diselenacyclohex-3-ene (32b). As in the synthesis of **1g**, method III, **31b** (0.5 mmol, 175 mg) in THF (3 mL) was treated with TBAF (0.5 mmol) in THF (15 mL). Chromatography (hexane) gave **32b** (120 mg, 77%), a red oil; ^{1}H

NMR δ 6.08 (t, J = 7.0 Hz, 1H), 3.28 (d, J = 7.0 Hz, 2H), 1.83 (s, 3H), 1.75 (s, 3H), 1.20 (s, 9H); ^{13}C NMR δ 156.23, 132.21, 128.10, 124.58, 38.94, 37.10, 29.36, 26.04, 21.83; ^{77}Se NMR δ 414.6, 286.8; EI-GC-MS *m/z* 310 (M^+, 11%), 229 (24%), 173 (52%), 57 (100%); UV (CH_2Cl_2) λ_{max} 414 (ε 190), 260 (ε 2666), 236 nm (ε 2790).

2,5-Bis(isopropylidene)thiolane (33a)[19c]. As in the synthesis of **22a** and **25a**, sulfur dichloride (1.2 mmol, 0.12 g) was added slowly at -70 °C to a solution prepared from Ti(O*i*-Pr)$_4$ (1.2 mmol, 0.40 mL) in ether (10 mL), 3,3-dimethyl-1,2-butadiene (**26**, 2.0 mmol, 0.20 mL) and *i*-PrMgCl (2.4 mmol, 1.2 mL, 2.0 M in ether) at -78 °C. After workup, chromatography (hexane) gave the known **33a** as a white solid (0.14 g, 85%). ^{1}H NMR δ 2.60 (s, 12H), 1.71 (s, 4H); ^{13}C NMR δ 131.05, 121.89, 25.32, 19.90; GC-MS *m/z* 168 (M^+), 153, 137, 125, 111, 97, 85, 77, 67, 59.

2,5-Bis(isopropyl)thiophene (3h).[19d] Compound **33a** was isomerized by a trace of acid to **3h**. ^{1}H NMR δ 6.57 (s, 2H), 3.09 (m, J = 6.7 Hz, 2H), 1.28 (d, J = 6.7 Hz, 12H); ^{13}C NMR δ 150.22, 120.97, 29.95, 24.69; GC-MS *m/z* 168 (M^+), 153, 138, 125, 119, 111, 97, 91, 77, 59, 53.

2,5-Bis(isopropylidene)selenolane (33b). As in the synthesis of **22a** and **25a**, selenium diselenocyanate (1.0 mmol, 0.30 g) in CH_2Cl_2 (5 mL) was added slowly at -70 °C to a solution prepared from Ti(O*i*-Pr)$_4$ (1.2 mmol, 0.40 mL) in ether (10 mL), 3,3-dimethyl-1,2-butadiene (2.0 mmol, 0.20 mL) and *i*-PrMgCl (2.4 mmol, 1.2 mL, 2.0 M in ether) at -78 °C. After workup, chromatography (hexane) gave **33b** as a light yellow solid (0.19 g, 88%) identical with that characterized as a side product in synthesis of **30b**.

2,5-Bis(isopropyl)selenophene (34). Compound **33b** was isomerized by a trace of acid to **34**. ^{1}H NMR δ 6.75 (s, 2H), 3.15 (m, J = 6.8 Hz, 2H), 1.31 (d, J = 6.8 Hz, 12H); ^{13}C NMR δ 158.16, 123.14, 32.39, 25.52; ^{77}Se δ 557; EI-GC-MS *m/z* 216 (M^+), 201, 173, 120, 105, 91, 77, 53.

Gas-Phase Pyrolysis of 1,2-Dithiin (1c) and 1,2-Diselenin (5a). Dilute solutions of **1c** and **5a** were introduced into the injection port of a GC-MS. At an injection port temperature of 150 °C, compounds **1c** and **5a** were unchanged, giving single peaks with molecular ions of *m/z* 114 and 212, respectively. At injection port temperatures of 200 °C **1c** gives a mixture **1c** and a new compound, **40** (*m/z* 114), along with small amounts of a longer retention time compound with *m/z* 230 (corresponds to 2 × 114 –2). When the injection port temperature is increased to 300 °C the peak for **1c** is completely replaced by the peak for **40**. Flash vacuum pyrolysis of **1c** at 500 °C afforded a foul smelling liquid identified as 2-thiophenethiol (**40**) by comparison with an authentic sample:[29] At an injection port temperature of 200 °C **5a** gives a mixture **5a** and selenophene (**44**), identified by comparison with an authentic sample. When the injection port temperature is increased to 300 °C the peak for **5a** is completely replaced by the peak for **44**.